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(54) Title: CERAMIC MATERIALS FOR THE MANUFACTURE OF REFRACTORY ROLLERS AND OTHER SUPPORTS

(57) Abstract

The invention relates to the use of ceramic materials containing a crystalline phase generically defined as "oxide" and consisting of at least one metal, one semi–metal or one non–metal such as phosphorus, arsenic, carbon and selenium bonded chemically to oxygen, and represented for example by silicates such as mullite and/or cordierite, and a phase defined as "non–oxide" and consisting of compounds of the type comprising carbides and/or nitrides of metallic and/or semi–metallic elements, and/or of metals such as aluminium and nickel and/or metal alloys such as nickel, cobalt or aluminium alloys, and/or steels. Such oxide/non–oxide ceramic materials containing the oxide and non–oxide phases in predetermined proportion are used for manufacturing ceramic products such as refractory ceramic rollers and other extruded supports for industrial firing kilns. The ceramic products obtained in this manner possess considerable properties which can solve those particularly severe situations which arise in the operation of industrial kilns such as deformation and insufficient resistance due to temperature changes. The refractory ceramic rollers and the other extruded refractory supports produced using the oxide/non–oxide ceramic material are also claimed as such, as is the process for their preparation.

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CERAMIC MATERIALS FOR THE MANUFACTURE OF REFRACTORY ROLLERS AND OTHER SUPPORTS.

This invention relates to ceramic materials containing "oxides", for example cordierite $(Mg,Fe)_2Al_4Si_5O_{18}$ and/or mullite $3Al_2O_3.2SiO_2$ together with "non-oxides", for example carbides and/or nitrides of various types intended, in particular, for the manufacture of refractory ceramic rollers and other extruded supports.

Roller kilns for firing tiles have been used with excellent results for about a quarter of a century. During the years technical improvements in the kiln structure and ceramic materials have enabled the roller diameter to be reduced (20-25 mm) and their length to be increased (up to 5 m), to achieve ever increasing production in such kilns. The main advantage of this technology is the high level of mechanization which can be applied in all processing stages of the material treated in these kilns.

This advantage results in remarkable economical and operating benefits. Roller kilns are currently used not only for firing tiles but also for the most diverse applications and severe production conditions in terms of supported loads, such as the firing of sanitary appliances, stoneware pipes and clinker. In this type of kiln, the material to be fired slides on a bed of rollers driven to rotate about their axis. The material is hence conveyed as on a conveyor belt from the preheating region, where the temperature is gradually increased (for example to 800-1000°C)

to those regions in which the temperature is a maximum (for example up to 900–1300°C), the material undergoing process transformation to reach the rapid cooling region, in which along just a few linear metres of kiln it is rapidly cooled, to reach the kiln exit region. All the refractory ceramics used in these kilns must possess adequate physical, chemical and mechanical characteristics for the particular use for which they are intended. For example, the basic requirements for the ceramic rollers used in these kilns include narrow dimensional tolerances, maintenance of rectilinearity in all kiln regions, good mechanical resistance to bending at high temperature, indeformability even if considerable temperature turbulence is present, good resistance to temperature change, and good chemical resistance in environments which are fairly aggressive because of the high temperature of the vapours present.

Other refractory ceramic products are also known, used as industrial refractory kiln supports and equipment of various forms and function, such as bricks, fibres, burner nozzles, bars and refractory plates, or heat exchanger tubes and blowers. These products must offer considerable chemical, physical and mechanical stability, including at high utilization temperatures. Such production, in all the constituent stages of the production cycle (shaping, drying, firing, finishing), in its currently known various forms and modes of operation (extrusion, pressing, normal and pressure casting), is well known to the expert of the art.

Ceramic products based on cordierite and/or mullite are known, in which these minerals are often associated with corundum, zirconium silicate and other synthetic phases known to the expert of the art. Cordierite and mullite are known to be used in those ceramics pertaining to the family of traditional acid and basic technical ceramics and are processed by classical firing techniques.

Finally, carbide and/or nitride–based ceramic products are known in which these phases are often associated with each other, with

metals, with alloys and with other synthetic ceramic phases known to the expert of the art. These phases are known to be used to obtain ceramic materials pertaining to the family of so-called "non-oxides" and require particular control, both of their chemical composition and of the process parameters for manufacturing the ceramic products containing them.

In this description and in the subsequent claims, the term "ceramic material" means a synthetic material obtained by sintering inorganic powders at high temperature and having a prevalently crystalline structure comprising one or more phases, the term "ceramic product" means a manufactured product for industrial use having a piece-wise or powder granulate format consisting essentially of ceramic material, and the term "oxide" means any phase forming part of a chemically stable and inert ceramic material having a crystalline structure at temperatures between ambient temperature and those temperatures at which industrial kilns usually operate, and consisting of at least one metal, one semi-metal or one non-metal (S.I. Tompkieff, "A New Periodic Table of the Elements", London, Chapman and Hall, 1954) such as phosphorus, arsenic, carbon and selenium, bonded chemically to oxygen.

The scope of this definition includes for example silica and all those crystalline phases which mineralogically pertain to silicates (eg. mullite and cordierite), calcium and magnesium carbonates, spinel, calcium, magnesium and aluminium phosphates, corundum, zircon, rutile etc. A large series of materials which satisfy the aforesaid "oxide" definition and which generally form part of the phases used in the implementation of this invention can be obtained from the book by M. Fleisher and J.A. Mandarino "Glossary of Mineral Species 1991", 6th Ed. 1991, The Mineralogical Record Inc., Tucson.

In this description and in the subsequent claims, the term "non-oxide" identifies compounds of ionic, covalent or metallic type of crystalline structure, chemically stable and inert under

industrial kiln operating conditions, which form at high temperature between carbon and metallic or semi-metallic elements (carbides), compounds of ionic, covalent or metallic type of crystalline structure, chemically stable and inert under industrial kiln operating conditions, which form at high temperature between nitrogen and metals or semi-metals (nitrides), and inert metals and/or metal alloys resistant to the high temperatures usually used in industrial kilns. Typical examples of carbides which can be used in the implementation of this invention are chromium, aluminium, silicon, titanium, iron, nickel, manganese, zirconium, vanadium, molybdenum, tantalum, boron and tungsten carbides. Typical examples of nitrides which can be used in the implementation of this invention are chromium, aluminium, silicon, titanium, zirconium, vanadium, molybdenum, tantalum and boron nitrides. Typical examples of metals which can be used in the implementation of this invention are aluminium and nickel. Typical examples of metal alloys which can be used in the implementation of this invention are alloys based on nickel or cobalt, cupro-nickel alloys, iron, magnesium and aluminium alloys, monel alloys and steels.

The term "oxide/non-oxide ceramic material" means a ceramic material in which at least one "oxide" (and hence, as stated heretofore, phases known to be used in the traditional technical ceramics industry) and at least one "non-oxide" (and hence phases known to be used in the advanced technical ceramics industry) are used jointly in predetermined ratios and processed such as to form a mixture of crystalline phases comprising at least one oxide and at least one non-oxide which constitutes the essential part of the ceramic material of which the ceramic products of this invention are composed. The term "essential part" identifies herein that portion of the ceramic material which is responsible for the particular physical, mechanical and chemical characteristics imparted to the ceramic products obtained by the methods of this invention.

In the composition of said products the phases forming the

oxide/non-oxide ceramic materials can be accompanied by other phases subsidiary to said mixtures.

The presence of these subsidiary phases, which can be present in non-crystalline form (eg. vitreous), can be considered useful but not necessary in the implementation of this invention.

A typical example of a ceramic product formed in accordance with this invention can consist of an oxide/non-oxide ceramic material formed from a mixture of cordierite (and/or mullite) and carbide (and/or nitride) optionally accompanied by one or more subsidiary phases.

This invention, when applied to the ceramic refractories field, enables a new range of ceramic products with special properties to be developed, able to solve not only the more common problems but also particularly severe technical ceramic problems such as high deformability of the refractory ceramic rollers in the rapid cooling region of roller kilns, and the insufficient resistance of the refractory support plates to the temperature changes to which they are subjected under certain conditions of use.

The main provision of this invention, which is based on the use of ceramic material in which at least a portion consists of oxide/non-oxide ceramic material, enables ceramic products which are of innovative type in terms of their functional characteristics to be obtained, in particular refractory ceramic rollers for industrial firing kilns, ceramic products formed by extrusion and/or drawing such as refractory plates, and kiln parts of various dimensions preferably lightened by cellular sections of different design and cross-section. These products also form part, as such, of this invention.

According to the method of this invention, using stoichiometric criteria, the mix of materials of oxide and non-oxide type to be processed to obtain an oxide/non-oxide ceramic material in which the two types of components of the mixture are present in the

desired proportions is firstly determined.

According to a preferred embodiment of the invention the ceramic material used to obtain the aforesaid ceramic products contains a portion of at least 50% of oxide/non-oxide ceramic material, any remainder being formed of subsidiary phases as indicated heretofore.

The oxide/non-oxide ceramic material preferably consists of mullite ($3Al_2O_3.2SiO_3$) and/or cordierite $(Mg,Fe)_2Al_4Si_5O_{18}$ as the oxide, and silicon carbide and/or titanium and/or boron and/or silicon nitride as the non-oxide. The ratio of oxide to non-oxide can vary from 1:9 to 9:1 by weight, preferably from 1:3 to 3:1 by weight.

For example, to produce by traditional processes ceramic products of this invention consisting entirely of oxide/non-oxide two-phase ceramic material formed from mullite ($3Al_2O_3.2SiO_3$) and titanium carbide (TiC) in the following weight proportions: 30% mullite-70% TiC, 50% mullite-50% TiC and 70% mullite-30% TiC, a mix must be prepared having the total chemical compositions expressed in Table 1. These can be achieved by inserting titanium carbide in the established proportion into a mixture of traditional raw materials (aluminas, clays, kaolins) which satisfy the chemical composition ratios given in Table 1. This oxide/non-oxide ceramic material can be synthesized by firing procedures varying from a few hours to 100 hours and can reach maximum temperatures of between 1300 and 1700°C.

TABLE 1

	Chemical composition (weight)		
	TiC%	SiO_2%	Al_2O_3%
A) 30% mullite - 70% TiC	70	8.5	21.5
B) 50% mullite - 50% TiC	50	14	36
C) 70% mullite - 30% TiC	30	19.7	50.3

To produce ceramic products consisting entirely of two-phase oxide/non-oxide ceramic material formed from cordierite ($Mg_2Al_4Si_5O_{18}$) and silicon carbide (SiC) in the following weight proportions: 30% cordierite-70% SiC, 50% cordierite-50% SiC and 70% cordierite-30% SiC, a mix must be prepared having the total chemical compositions expressed in Table 2. These can be achieved by inserting silicon carbide in the desired proportion into a mixture of traditional raw materials (talcs, chlorites, aluminas, clays, kaolins) which satisfy the chemical composition ratios given in Table 2. This oxide/non-oxide ceramic material can be synthesized by firing procedures generally lasting from a few hours to 100 hours and can reach maximum temperatures of between 1100 and 1400°C.

TABLE 2

	Chemical composition (weight)			
	SiC%	MgO%	SiO_2%	Al_2O_3%
D) 30% cordierite - 70% SiC	70	4.1	15.4	10.5
E) 50% cordierite - 50% SiC	50	6.9	25.6	17.5
F) 70% cordierite - 30% SiC	30	9.7	35.9	24.4

The mix preparation operations are effected in accordance with known methods in the technical branch to which this invention relates. For example, the raw materials defining the ceramic material composition are measured out and mixed by known methods, firstly dry and then wet, for a time sufficient to ensure homogenization. The mix obtained in this manner is then extruded into pieces of desired shape and length or cast or pressed. The pieces obtained in this manner are dried by placing them on suitable supports or frames in dryers at a temperature of the order of 100°C. The dried products are then placed in kilns for their firing. This latter is carried out by applying different temperature gradients and residence times at various temperatures, depending on the different products to be obtained and the

different raw materials used, temperatures exceeding 1100°C being in any event always required.

By way of example, Table 3 shows the heat treatment times and relative temperatures of each of the mixtures A), B) and C) for obtaining ceramic products of the invention in the form of refractory ceramic rollers for industrial kilns.

TABLE 3

A		B		C	
Temperature	gradient °C/hour	Temperature	gradient °C/hour	Temperature	gradient °C/hour
700	50	700	50	700	50
1250	100	1250	100	1250	100
1400	50	1400	50	1400	50
1600	25	1500	25	1450	25
hours residence at maximum temperature	5	hours residence at maximum temperature	10	hours residence at maximum temperature	15

TABLE 4

D		E		F	
Temperature	gradient °C/hour	Temperature	gradient °C/hour	Temperature	gradient °C/hour
500	50	700	50	700	50
1250	100	1250	100	1250	100
1360	50	1360	50	1320	50
hours residence at maximum temperature	3	hours residence at maximum temperature	4	hours residence at maximum temperature	5

By way of example, Table 4 shows the heat treatment times and relative temperatures of each of the mixtures D), E) and F) for obtaining ceramic products of the invention in the form of refractory ceramic rollers for industrial kilns.

Firing plates with cellular sections formed from oxide/non-oxide ceramic materials of composition A), B), C), D), E) or F) can be

obtained by applying essentially the heat treatments represented in Tables 3 and 4.

It should be noted that the conditions represented in Tables 3 and 4 are suitable for forming ceramic products falling within the scope of this invention starting from materials of traditional type, and are purely indicative in that the specific conditions are determined in each particular case on the basis of the experience of the expert of the art and on the basis of the composition and chemical and physical characteristics of each material or combination of starting materials used and the composition of the final ceramic product to be obtained.

Particular attention must be dedicated to the process temperature in those cases in which alloys are used as non-oxide components of the oxide/non-oxide ceramic material. If the alloy is the main component, the process temperatures must be very close to those of the metallurgical processes (eg. an aluminium alloy reinforced with silicon carbide). If the alloy is a secondary component the melting point can be exceeded to generate within the ceramic a molten phase which solidifies during cooling.

This invention, when applied to the field of refractory ceramics, enables a new range of materials with special properties to be developed, able to solve not only the more common problems but also particularly severe situations such as high deformability of the refractory ceramic rollers in the rapid cooling region of roller kilns, the insufficient resistance of the refractory support plates to the temperature changes to which they are subjected under certain conditions of use, or the need for rapid heat transfer which represents the most desirable characteristic in certain particular ceramic products.

The use of oxide/non-oxide ceramic materials in the aforesaid applications constitutes the essential characteristic of the invention claimed herein, the scope of which also comprises the ceramic products obtained by this use and their manufacturing process.

Claims:

1. Use of oxide/non-oxide ceramic materials for obtaining ceramic products consisting of refractory ceramic rollers and other extruded refractory supports for industrial firing kilns.

2. Use of oxide/non-oxide ceramic materials as claimed in claim 1, wherein the materials of oxide type are chosen from silica and all those crystalline phases which pertain to silicates, preferably mullite and/or cordierite, calcium and magnesium carbonates, calcium, magnesium and aluminium phosphates, spinel, corundum, zircon and rutile; the materials of non-oxide type being chosen from chromium, aluminium, silicon, titanium, iron, nickel, manganese, zirconium, vanadium, molybdenum, tantalum, boron and tungsten carbides, chromium, aluminium, silicon, titanium, zirconium, vanadium, molybdenum, tantalum and boron nitrides, metals such as aluminium and nickel, metal alloys based on nickel or cobalt, cupro-nickel alloys, iron, magnesium and aluminium alloys, monel alloys and steels.

3. Use of oxide/non-oxide ceramic materials as claimed in claims 1 and 2, wherein the phases constituting said materials are accompanied by other subsidiary phases, which can be present in crystalline or vitreous form.

4. Use of oxide/non-oxide ceramic materials as claimed in claim 3, wherein the ceramic product obtained contains at least 50 wt% of oxide/non-oxide ceramic material, the ratio of oxide to non-oxide varying from 1:9 to 9:1 by weight, preferably from 1:3 to 3:1 by weight.

5. Use of oxide/non-oxide ceramic materials as claimed in claims 1 to 4, wherein the oxide/non-oxide ceramic material consists of mullite and/or cordierite as the oxide, and silicon carbide and/or titanium and/or boron and/or silicon nitride as the non-oxide.

6. Use of oxide/non-oxide ceramic materials as claimed in claims 1 to 5, for forming refractory ceramic rollers for industrial firing kilns.

7. Use of oxide/non-oxide ceramic materials for forming extruded ceramic supports, preferably refractory plates and extruded kiln parts with cellular sections of various design or cross-section for industrial firing kilns.

8. A ceramic product formed from ceramic material comprising at least 50 wt% of oxide/non-oxide ceramic material, characterised in that said ceramic product is a refractory ceramic roller or other extruded refractory support for industrial firing kilns.

9. A ceramic product as claimed in claim 8, being a refractory ceramic roller for industrial firing kilns.

10. A ceramic product as claimed in claim 8, being a plate or an extruded kiln part with cellular sections of various design and cross-section for industrial firing kilns.

11. A ceramic product as claimed in claims 8 to 10, characterised in that the oxide/non-oxide ceramic material consists of a mixture of at least one phase qualifiable as oxide and at least one phase qualifiable as non-oxide, the ratio of the oxide phase (or phases) to the non-oxide phase (or phases) having a predetermined value varying within the range from 1:9 to 9:1 by weight, preferably from 1:3 to 3:1 by weight, said oxide/non-oxide ceramic material optionally being accompanied by other subsidiary phases in crystalline and/or vitreous form.

12. A ceramic product as claimed in claims 8 to 11, characterised in that the oxide/non-oxide ceramic material is formed from material of oxide type chosen from silica and all those crystalline phases which pertain to silicates, preferably mullite and/or cordierite, calcium and magnesium carbonates, calcium, magnesium and aluminium phosphates, spinel, corundum,

zircon and rutile; the materials of non-oxide type being chosen from chromium, aluminium, silicon, titanium, iron, nickel, manganese, zirconium, vanadium, molybdenum, tantalum, boron and tungsten carbides, chromium, aluminium, silicon, titanium, zirconium, vanadium, molybdenum, tantalum and boron nitrides, metals such as aluminium and nickel, metal alloys based on nickel or cobalt, cupro-nickel alloys, iron, magnesium and aluminium alloys, monel alloys and steels.

13. A ceramic product as claimed in claims 8 to 12, characterised in that the oxide/non-oxide ceramic material consists of mullite and/or cordierite as the oxide, and silicon carbide and/or titanium and/or boron and/or silicon nitride as the non-oxide.

14. A process for preparing a ceramic product based on oxide/non-oxide ceramic material and consisting of refractory ceramic rollers or other extruded supports for industrial firing kilns, comprising the steps of proportioning the raw materials defining the ceramic material, preparing the mix, shaping and heat treating the product, characterised in that the starting materials for forming the oxide and non-oxide phases of the oxide/non-oxide ceramic material are combined in quantities predetermined on the basis of their chemical composition, the chemical composition of the oxide phase or phases and of the non-oxide phase or phases which are to constitute the oxide/non-oxide ceramic material, and the respective proportions of these phases in said material.

15. A process as claimed in claim 14, wherein the raw materials are chosen from alumina, clay and kaolin, the oxide phase being formed from mullite and the non-oxide phase consisting of titanium carbide, their ratio in the synthesized ceramic material varying from 1:3 to 3:1 by weight.

16. A process as claimed in claim 14, wherein the raw materials are chosen from talc, chlorite, alumina, clay and kaolin, the oxide phase being formed from cordierite and the non-

oxide phase consisting of silicon carbide, their ratio in the synthesized ceramic material varying from 1:3 to 3:1.

17. A process as claimed in claim 15, wherein the duration of the firing stage varies from a few hours to 100 hours and the maximum temperature attained is between 1300 and 1700°C.

18. A process as claimed in claim 16, wherein the duration of the firing stage varies from a few hours to 100 hours and the maximum temperature attained is between 1100 and 1450°C.

INTERNATIONAL SEARCH REPORT

Inte[illegible]onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 89 05285 A (DURIRON CO) 15 June 1989 see page 33, line 6 - page 34, line 32 see page 3, line 3 - line 6 see example 6 ---	1-5,7,8, 10-14, 16,18 15,17
X A	WO 95 33965 A (SIRMA NUOVA ;SCHOENNAHL JACQUES PAUL RAYMON (FR)) 14 December 1995 see claims 1,10 see page 2, line 10 - line 26 see page 5, line 35 - page 6, line 11 --- -/--	1-6,8,9, 11-14,16

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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